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Article

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Elevated trimethylarsine oxide (TMAO) and inorganic arsenic in northern hemisphere summer monsoonal wet deposition.

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Abstract

Arsenic speciation, their inputs, for wet deposition are not well understood. Here we demonstrate that trimethylarsine oxide (TMAO) and inorganic arsenic are the dominant species in monsoonal wet deposition in summer Indian subcontinent, Bangladesh, with inorganic arsenic dominating, accounting for ~80% of total arsenic in this medium. Lower concentrations of both species were found in monsoonal wet deposition in the winter Indian subcontinent, Sri Lanka. The only other species present was dimethylarsinic acid (DMAA), but this was usually below limits of detection (LoD). We hypothesize that TMAO and inorganic arsenic in monsoonal wet deposition is predominantly of marine origin. For TMAO, the potential source is the atmospheric oxidation of marine derived trimethylarsine. For inorganic arsenic, our evidence suggests entrainment of water column inorganic arsenic into atmospheric particulates. These conclusions are based on weather trajectory analysis, and to the strong correlations with known wet deposition marine derived elements: boron, iodine and

selenium. The finding that TMAO and inorganic arsenic are widely present, and elevated in monsoonal wet deposition identifies major knowledge gaps that need to be addressed regarding understanding arsenic's global cycle.

Introduction

Atmospheric fluxes, with respect to the global cycling, of arsenic are poorly characterized (1). Arsenic species in wet deposition have been particularly neglected, with the exception of studies of Huang and Matzner (2) who systematically quantified inorganic and methylated arsenic species inputs into terrestrial systems, whereas, with most wet (and dry) deposition studies simply determining total arsenic inputs (3-7). Huang and Matzner found that the only organic species detected in bulk deposition for a German forest catchment was trimethylarsine oxide (TMAO), but with the majority of measurements below limits of detection (<LoD) (2). Monomethylarsonic acid (MMAA) and dimethylarsinic acid (DMAA) were below LoD for bulk deposition, but with some samples detected above LoD in throughfall, which was attributed to phyllosphere microbes methylating inorganic arsenic. Inorganic arsenic was measured in much higher concentrations than methylated species, by 10-20-fold, both in bulk deposition and in throughfall. TMAO and DMAA have been better studied in atmospheric particulates where they are routinely detected (8-10). The origin of these species in particulate samples is attributed to the biovolatilization of trimethylarsine (TMA) and dimethylarsine (DMA) from soils (10), mediated by arsenic methylating bacteria and fungi (11), with subsequent UV oxidation of these atmospherically unstable arsines to their corresponding oxides, TMAO and DMAA (12). Recently, using online atmospheric pressure chemical ionization, TMA, along with inorganic arsenic, was shown to be the dominant gaseous arsenic species in remote Finnish ecosystems, showing a strong

61 relationship to melting of snow cover and stimulated activity of arsenic-methylating
62 microorganisms (13).
63
64 Inorganic arsenic is also not widely characterized in wet deposition, again with the most
65 detailed study conducted by Huang and Matzner (2). Studies on total arsenic deposition,
66 historically (1, 3-6), and more recently (5,7), conclude that arsenic is predominantly from
67 industrial sources. Historically, starting from when arsenic in deposition was first measured,
68 this may have been the case, but inputs of total arsenic in wet deposition have been falling
69 rapidly at long-term monitoring sites (5), attributed to less base and precious metal mining in
70 historic areas of activity and to stricter environmental regulations (14). Source appointment
71 of total arsenic in deposition is normally complex due to multiple potential inputs and to
72 shifting weather trajectories (15). However, the fact that the industrial baseline input is
73 declining (14) should make the study of natural geogenic or biogenogenic arsenic inputs into
74 the atmosphere easier to address. This study of geogenic/biogenic inputs is also aided by
75 the analytical advances that have enabled arsine effluxes from habitats to be quantified (16).
76
77 This study was to investigate wet depositional arsenic species inputs, and to identify the
78 sources of these inputs, in monsoonal settings. Sites in Bangladesh and Sri Lanka were
79 chosen because of the relatively unpolluted nature of the Indian Ocean and connected
80 landmasses, far from the major global anthropogenic sources of arsenic atmospheric pollution
81 (14,15). Also, monsoonal systems have relatively simple weather trajectories (17), which
82 enables straightforward source appointment. The findings are interpreted in light of the
83 current state-of-knowledge regarding atmospheric fluxes within arsenic's biogeochemical
84 cycle (1,3), indicating that this is limited and not well understood, and that this cycle needs to
85 be rethought due to the findings presented here.

86

87 **Materials and Methods**

88 Details of manufacturers of sampling equipment, instrument manufacturers and reagents are
89 given in Table S1. Sampling took place at Mymensingh, Bangladesh, 24°45'N, 90°24'E
90 (Figure 1) and at Matara, Sri Lanka, 5°57'N, 80°31'E (Figure 1). Bangladesh samples (n=38)
91 were collected during the summer monsoon of 2016, and Sri Lankan samples (n=17) during
92 the winter monsoon that followed. Only wet deposition samples were collected, with
93 sampling undertaken in triplicate, using pre-weighed 56 mm diameter polypropylene
94 containers, over a 24-h period, and immediate freezing until subsequent analysis. The
95 containers were on a small platform 1.5 m above the terrain surface in an open position.
96 Containers were weighed to calculate the volume of water deposited on a surface area basis.

97

98 For elemental quantification, samples were 0.45 micron filtered, before being acidified with
99 ultra-high purity (Aristar[®]) nitric acid (0.1 M), with the exception of iodine, where
100 tetramethylammonium hydroxide (0.5%) was added instead. The internal standard added
101 throughout was rhodium, spiked to give a 10 µg/l concentration. For the determination of
102 arsenic species, using a similar ion exchange- ICP-MS approach as Huang and Matzner (2),
103 samples were 0.45 micron filtered before analysis by ion-exchange - ICP-MS, using a
104 Thermo Scientific IC5000 Ion Chromatography system coupled with a Thermo ICAP-Q ICP-
105 MS. A 2x250mm Thermo Scientific AS7 anion-exchange column was used with a 2x50mm
106 AG7 guard column and ammonium carbonate over a linear gradient from 20nM to 200nM
107 was the mobile phase. Authentic standards of arsenobetaine, inorganic arsenic, MMAA,
108 DMAA, and TMAO were run to ascertain retention times. The Thermo Scientific ICAP-Q
109 ICP-MS in helium collision cell mode was used for the analysis of all elements analyzed,
110 with the exception of boron which was run in standard mode (no collision cell). To validate

the AS7 identification, a subset of samples was also analyzed by cation-exchange chromatography and run on a 2x250mm Thermo Scientific CS12A column, with a 2x50mm CG12A guard column. Pyridine mobile phase (20mM) was made up and buffered to pH 2.6 with formic acid for isocratic analysis and TMAO was spiked into authentic samples for both columns.

For all analytical methods, blanks were prepared from $>18.2 \text{ M}\Omega\cdot\text{cm}$ (at 25°C) water in the same manner as the samples and included with each instrument batch. LoD was calculated as average concentration of the blank + 3 times standard deviation of a species mix dilution series. For arsenic speciation and total elemental analysis a synthetic surface water CRM was run. Only inorganic arsenic was present to quantify. For a subsample of unknowns, iodine was spiked into samples prepared for TMAH analysis, which could then be compared to the corresponding unspiked samples and a percentage recovery calculated.

To determine either the origin of rain, or the source of air that will form rain through orographic lifting, 72-h backward air trajectories were calculated for each day using Hysplit software and the Global Data Assimilation System (18). All statistical analysis was conducted in IBM SPSS (Version 22). Normality of residuals were checked for parametric analysis, and if not normal, non-parametric analysis, and reporting of medians, was conducted.

Results

Representative chromatograms for monsoonal wet deposition samples for both AS7 and CS12A columns are given in Figure S1, with spikes and authentic samples showing that TMAO was present, along with DMAA and inorganic arsenic. MMAA and AsB were below

LoD. The LoDs for arsenic species were 0.117, 0.128 and 0.278 nM for DMAA, TMAO and inorganic arsenic, respectively, the highest LoD of the two batches of sample runs. Half LoD, was used where samples were <LoD for statistical analysis. For arsenic speciation, average percentage recovery of inorganic arsenic from the CRM's was 110%, n=5 (Table S2). For the full-scan analysis, the same CRM was prepared in triplicate for each batch with the individual elemental average recoveries ranging from 89 to 122%, with the average iodine recovery from spiked samples being 98%, n=6.

As Bangladesh was sampled through the whole of the monsoonal season, unlike Sri Lanka where only a month of monsoonal wet deposition was collected, the seasonal input of arsenic species into Bangladesh soils could be determined. This was 2.3 g/ha for inorganic arsenic, and 0.4 g/ha for TMAO (Figure 2). DMAA was not included in subsequent correlation analysis as it was primarily below LoD.

The 72-h weather trajectories for wet deposition sampling dates originated from the northern Indian Ocean, the Bay of Bengal, and the Gulf of Arabia for both the summer and winter monsoons (Figure 1). Median TMAO concentrations in Bangladeshi wet deposition were 0.30 nM compared to 0.056 nM, the $\frac{1}{2}$ LoD, for Sri Lanka (Figure 3). Median DMAA were both at the LoD for Bangladesh and Sri Lanka (data not shown), while inorganic arsenic was 1.33 and 0.33 nM, for the Bangladesh and Sri Lanka, respectively (Figure 3). Inorganic arsenic concentrations in wet deposition were ~5-fold higher than organic concentrations, for both Bangladesh and Sri Lanka (Figure 3).

Relationships between other elements and TMAO (Figure 3) and inorganic arsenic (Figure 4), and with wet deposition volume (Figure 5) and distance from origin of 72-h weather

trajectories (Figure S2) were analyzed by Spearman's correlation (Table S3) for the Bangladeshi and Sri Lankan data sets. Spearman's correlation showed for Bangladesh that TMAO correlated well with boron ($P < 0.001$), selenium ($P < 0.001$), strontium ($P < 0.001$) and chromium ($P < 0.001$), and to a lesser extent with iodine ($P = 0.035$), cobalt ($P = 0.02$), rubidium ($P = 0.015$) and cadmium ($P = 0.028$). It was also negatively correlated with wet deposition volume ($P = 0.031$). TMAO was poorly correlated with inorganic arsenic ($P = 0.525$), length of trajectory ($P = 0.846$), and with copper ($P = 0.113$), barium ($P = 0.479$) and lead ($P = 0.299$), amongst other elements. For inorganic arsenic in wet deposition there were similarities and differences to TMAO (Table S3). Inorganic arsenic was, similar to TMAO, positively correlated with iodine ($P = 0.001$), selenium ($P < 0.001$), and had a poor correlation with copper ($P = 0.148$), and was not correlated with trajectory length ($P = 0.069$). In contrast to TMAO, inorganic arsenic had a very strong negative correlation with barium ($P < 0.001$), was positively correlated with lead ($P = 0.019$), and was not correlated with deposition volume ($P = 0.621$), boron ($P = 0.135$) and cadmium ($P = 0.413$), amongst other elements. Correlations for the Sri Lankan data (Table S3) were less significant throughout, as compared to the Bangladesh data set. TMAO and inorganic arsenic, for the Sri Lankan data, were only correlated with each other ($P = 0.001$), cadmium (TMAO, $P = 0.020$; inorganic arsenic, $P = 0.003$) and lead ($P = 0.001$ for both TMAO and inorganic arsenic).

179

Considering the two datasets together, there are highly significant ($P < 0.001$) negative correlations (Table S5) between wet deposition volume and rainwater concentrations of boron, selenium and cadmium, with iodine, chromium, iron and lead also showing washout (Figure 5). Distance to 72-h trajectory origin was only significant ($P = 0.036$) for barium. The Spearman's analysis showed that there were strong correlations between elements, other than arsenic species, for both Bangladesh and Sri Lanka (Table S3). This was true of elements that

will be primarily of marine origin such as selenium, iodine and boron, which show strong inter-correlations, while transition metals tend to correlate best with themselves. The elements that differ most between the two datasets, by an order of magnitude, are boron, selenium, cadmium and lead (Figures 3 and 4). For boron, selenium and cadmium, this can be explained at least partially by washout, with higher concentrations in Sri Lanka related to lower monsoonal wet deposition (Figure 5). For lead the reason why Sri Lankan data is ~10-fold lower than the Bangladeshi concentrations is not related to depositional volume.

All the sample points for Sri Lanka mapped to marine locations for their 72-h trajectory origin, but some of the Bangladeshi samples trajectories mapped them back to being in transects across the Indian sub-continental landmass (Figure 1). Kruskal-Wallis analysis found for every parameter measured, that there was no significant difference in concentrations in rain based on a Persian Gulf, continental Indian or Bay of Bengal 72-h trajectory origin (analysis not shown).

To interrogate the interrelationships between the data, Principle Components Analysis (PCA) was conducted, with the component factor score coefficient matrix as well as the individual sample scores (Figure 6). The Bangladesh and the Sri Lankan data followed different trends, outlined by ellipses, with these ellipses being orthogonal to each other, intersecting near the X-Y origin. The trends in these data suggest that there is a commonality in samples that co-locate at the origin, but that these differ towards the extremes of composition for the two data sets. The factor scores show that most elements pull to the right, with iodine, selenium and boron closely clustered, along with iron, manganese, chromium, cadmium, rubidium and strontium. Distance from origin and volume of water deposited also go along with this trend, with inorganic arsenic factor loadings most closely matching these.

Copper, cobalt, and less strongly lead, loadings are opposite to inorganic arsenic and orthogonal to most other elements. TMAO stands out by itself, diametric or orthogonal to all other elements, suggesting very different regulation.

Discussion

It was found that both inorganic arsenic and TMAO were elevated in the Bangladeshi summer monsoon wet deposition, as compared to Sri Lankan winter monsoon, and that TMAO made up ~20% of total arsenic deposited in both environs. DMAA was a minor component, with generally, levels below LoD. MMAA was not detected. TMAO concentrations were 4-fold higher in Bangladeshi wet deposition as compared to previous studies in a non-monsoonal continental setting, using their $\frac{1}{2}$ LoD (2), and equating to the Sri Lankan data. The TMAO also seems to be differentially regulated in wet deposition between the summer and winter Indian sub-continent monsoons, not correlated with inorganic arsenic during the summer, but highly correlated during the winter. To explain these findings the biology of TMAO production has to be considered in context of prevailing wind directions, and arsenic methylation in both marine and terrestrial settings.

TMAO

The origin of weather trajectories for both Bangladesh and Sri Lanka are both either the Bay of Bengal or the Persian Gulf, with a very similar origin distribution, except that some (36 %) Bangladeshi samples had 72-h weather origins that placed them as being in transit across India. However, Persian Gulf, Bay of Bengal and Indian mainland origin samples did not differ in any measured parameter for Bangladesh. Given that the Sri Lankan and Bangladeshi samples had similar marine origins but very different TMAO concentrations and associations with co-deposited elements, either the production of TMAO must differ at different times of

year, and/or the prevailing winds determine TMAO atmospheric loadings. As weather origins of the wet deposition are marine, and with an intercontinental convergence zone (ITZ) drawing air from the Indian Ocean in its northerly summer location, and from the continental landmass in its southern winter location (17), it may be expected, if TMA/TMAO is of terrestrial origin, that TMAO in wet deposition should be higher in the winter monsoon. This is not the case and the apparent marine source of TMA/TMAO is a conundrum.

TMA/TMAO production in terrestrial habits is fairly well established (16), but in marine habitats there is little evidence of it being present in environmental monitoring programmes where DMAA and MMAA are routinely detected (19,20), including the Persian Gulf and in the Indian Ocean just off the Sri Lankan shoreline (19). TMAO can be produced either through methylation of DMAA (16,11) or through degradation of the main marine arsenical, arsenobetaine (21). Previous maritime oxidized arsines monitoring, for atmospheric particulates sampled on the remote islands of the Japanese archipelago in the East China Sea, attributed their origin to the soils of the main Japanese islands, rather than the seas that surround Japan (10). In this Japanese investigation, as for our study, TMAO was the dominant organic species. They (10) argued against a marine source, but did not consider that marine water as a source of TMA/TMAO, even though the Japanese land surface is very small in comparison to its surrounding marine waters.

The fact that TMAO is not routinely measured in marine waters may be due to its absence, or more likely to concentrations being below LoD, in marine waters, and/or due to inappropriate analytical methodologies. The saline content of marine waters is challenging to most chromatographic conditions. Ion chromatography can separate the methylated species in waters but the TMAO LoD is much higher due to severe peak broadening under saline

conditions (data not shown). Most marine water studies for arsenic speciation use hydride generation (19,20), sometimes followed by pre-concentration (such as cryo-trapping), and these should pick up TMAO if present, as long as enough reductant is added as other moieties may be preferentially reduced, and as long as chromatographic runs are long enough to pick up late eluting TMA (22). When specific care was taken to speciate TMA/TMAO, where analytical limitations were overcome, ~0.2 nM TMAO concentrations were detected in 3 seawater certified reference materials (and 2 freshwater at similar concentrations), higher than MMAA (0.12 nM), 10-fold lower than DMAA (1.6 nM), and a 100-fold lower than inorganic arsenic (22). No such application of this type of analytical approach to actual environmental monitoring of TMAO in marine waters has been undertaken.

Even if TMAO is very low in waters, this does not preclude TMA volatilization and, indeed, loss of the trimethyl arsenic species through volatilization may itself explain why TMAO could be low in seawaters. No studies on marine water column arsenic biovolatilization have been conducted. Marine algae have been shown to biovolatilize arsenic in culture, though the volatilized forms were not speciated (11). DMAA can be observed above LoD in Bangladesh wet deposition, but not in Sri Lanka; and MMA is not found at all, presumably below LoD. As TMAO, it is assumed, is low in seawaters, the low DMAA and MMAA, which are routinely recorded in the Indian Ocean (19), and the high TMAO, argue against entrainment of seawater into atmospheric aerosols, as for boron (23), as being a major source. TMAO is highly correlated with boron, whose wet deposition source is marine derived sea spray, but it is also correlated with selenium and iodine that are marine biovolatilization derived in terrestrial wet deposition (24,25). As sources are mixed in wet deposition, care must be taken not to over interpret correlations (7,15).

Depositional rates can also be used to interpret potential inputs. The only previous TMAO, and indeed DMAA and MMAA, report known to us is a continental German study, with low (weekly) sampling resolution, where concentrations were generally below LoD (2). TMAO deposition in that continental setting was 0.05 g/ha/y, 10-fold lower than for Bangladesh. Dominant soil/sediment land-cover for Bangladesh, mangrove sediments and paddy soils, have all been shown to be amongst the highest producers of arsines so far measured, with TMA dominating (16). Total fluxes of arsines, including arsine, MMA, DMA and TMA, dominated by TMA, from Bangladesh paddy soil and coastal mangrove sediments were recorded in the field at 0.2 and 0.02 g/ha/y, respectively (16). This compares to 0.4 TMAO g/ha/y for wet depositional inputs measured for Bangladesh here over the monsoon period (Figure 2). While paddy ecosystem biovolatilization can contribute to TMAO inputs exceeding TMA outputs, this should be roughly the same for Bangladesh and Sri Lanka for wet deposition. As this is not the case, and that prevailing winds are from marine origin, it suggests that wet deposition TMAO is of both of terrestrial and marine origin. The reason why TMAO correlates with arsenic during the winter monsoon, but not during the summer, may be due to this interplay between terrestrial and marine sources, but this remains to be investigated. However, in an early study of arsenic speciation of surface waters in the northern Indian Ocean, and Persian Gulf off the Indian coast, MMAA concentrations decreased 6-fold, and DMAA 10-fold, during summer and winter (19). It appears that this corresponds to the considerable decrease in TMAO and DMAA in our wet depositional samples between the summer and winter monsoons, again pointing to a marine source for these elements in wet deposition.

TMAO in Bangladesh samples was not well correlated with industrial contaminants copper and lead that are normally associated with arsenic in ores (1-7), though it positively

correlated with cadmium. It was also not associated with inorganic arsenic which can have a strong anthropogenic signal, again originating from mining and smelting activity (1-7). For Sri Lankan samples, TMAO was correlated with lead and arsenic, as well as cadmium. As air masses are continental for the Sri Lankan winter monsoon, the correlation with lead, cadmium and arsenic may have a substantial terrestrial contribution. Lead is very high in Bangladeshi wet deposition, and cadmium in Sri Lankan. The reasons for these anomalies are not known. Inorganic arsenic can also be of marine origin, as outlined in the following section, and it may simply be that both inorganic arsenic and TMAO are predominantly of marine origin, but with different regulation: TMAO derived from biovolatilized TMA, and inorganic arsenic through aerosol entrainment. TMA can be UV-photodegraded (23), with TMA have a half-life of 7.2 h during the day (12). Thus, demethylation by photodegradation may reduce TMAO deposition from TMA generated during daytime. This further complexity in TMA/TMAO cycling may explain why the TMAO was orthogonal to all other arsenic species and other elements in the PCA analysis presented here.

Inorganic arsenic

The inorganic arsenic in wet deposition may be from multiple sources such as anthropogenic, volcanism and seawater entrainment into the atmosphere (1-3). The, relatively, much higher concentrations of inorganic arsenic in sea waters compared to wet deposition ~10-20 nM Persian Gulf/Indian Ocean waters, and 0.8 and 0.2 nM for wet deposition as reported for Bangladesh and Sri Lanka, respectively, suggests that physical transport, entrainment into the atmosphere from seawater as aerosols, may explain, at least partially, inorganic arsenic wet deposition concentrations, given that we have remote from industrial arsenic sources monitoring sites. The potential role of volatilization also needs consideration. Arsine (AsH_3), which is oxidized to its oxy anions in the atmosphere (12), is normally only a minor

component of volatilization from soils/sediments (16). Elevated arsine concentrations are found under highly reduced conditions (16), attributed to abiotic reduction. Such low oxygen tensions are not typical of epipelagic waters, potentially ruling out arsine volatilization from marine environments as a source. If volatilization was the dominant source of arsenic to wet deposition much higher levels of TMAO and DMAA, the oxidized products of methylated arsines, would be expected as compared to inorganic arsenic, as di- and tri- methylated arsines are the main species volatilized (16). As this is not the case, inorganic arsenic concentrations were ~5-fold higher than organic species, this again argues against volatilization being the primary source of inorganic arsenic. One proviso is that arsines, or their oxides, can be demethylated by UV. This has been exploited in hydride analysis where separated methylated species are UV cracked to overcome kinetic interferences in hydride generation (26).

Inorganic arsenic is highly negatively correlated with barium. Barium in wet deposition is normally attributed to terrestrial inputs (27). Studies on Barium fluxes into the Bay of Bengal show sharp clines away from deltaic zones towards the open oceans (28), again showing the strong terrestrial source of this elements in our study region. The negative correlation with barium for inorganic arsenic reported for Bangladesh here, is again strong evidence that, at least, marine sources are a strong contributor to monsoonal wet deposition of arsenic.

Wet deposition and arsenic's biogeochemical cycle

Historically, studies have attempted to attribute total arsenic in deposition to its sources, usually concluding them to be industrial (1-7). However, wet depositional inputs of arsenic decreased 5-fold from 1996 to 2010 in maritime Europe (5), with the authors of this report attributing this to rapidly declining anthropogenic inputs such as coal burning and metal

mining and processing. Studies using older deposition data (1,3,4,6) would not have been able to readily identify natural sources or arsenic against this industrial background. Furthermore, our study sites' weather patterns are predominantly marine, far from mining or industrial centres of activity. Both the modern timing, and the locations of our study has enabled us to better assess natural biogeochemical cycling of arsenic compared to previous investigations. A study in Britain, with more continental influenced weather patterns, found that total arsenic did have a strong marine signature when weather trajectories came from the marine west rather than the continent to the east (7). Also, early studies at lower sampling resolution and with measurement of total arsenic at coastal Pacific (6) and western Atlantic (4) locations also found strong marine contributions to wet deposition when weather trajectories were of oceanic rather than continental origin. A German study (2) that speciated arsenic in bulk deposition, sampling conducted in 2004-2005, found an inorganic arsenic deposition of 3.9 g/ha/y, similar to the Bangladesh location. Again, the German study is historic, and with deposition being predominantly from anthropogenic sources as prevailing winds cross major industrial zones.

Marine derived wet deposition of selenium (23) and iodine (24), biovolatilized by phytoplankton; and iodine (24) and boron (25), entrained into the atmosphere as aerosols through wind turbulence followed by evaporation, are the dominant sources of these elements to soils. For example, selenium deficiencies and sufficiencies in Chinese soils map to the northern limit of the monsoon (29). Total selenium concentrations in wet deposition are ~1-2 nM (29). Median inorganic arsenic concentrations in monsoonal Bangladesh deposition are 1.3 nM, *i.e.* with the range of selenium concentrations in wet deposition.

Using median As concentrations in wet deposition ranging from 0.23 to 1.75 nM for Sri Lanka and Bangladesh, respectively, and a global wet deposition of $5.1 \times 10^{14} \text{ m}^3/\text{y}$ (1), this equates to 9,000 – 69,000 t/y globally. While not all terrestrial landmass is monsoonal, most of the Earth's surface is marine, so this calculation may be considered as an upper boundary. Depositional inputs are assumed to be much lower in the southern as compared to the northern hemisphere (1), both our sites being in the north, but even so, our measurements suggest marine contribution to global arsenic deposition to be measured in the 10,000s per annum just on a northern hemisphere contribution. As it is estimated that 26,000-82,000 t/y of arsenic is deposited to the surface of the earth annually (1), marine sources are a major contribution to atmospheric inputs, if our assumption is correct that arsenic in wet deposition in monsoonal settings is marine derived. Matschullat (1), reviewing the available literature, estimated marine inputs of arsenic into the environment to be 27 t/y, 3-orders of magnitude lower than our estimates, although he cites older citations on maritime inputs that are in order with ours, 30,000-78,000 t/y (29). As these reviewed studies were based on old and limited analytical technologies, often with very limited actual measurements, Matschullat's argued that only further work to increase the reliability of global arsenic budgeting will resolves these discrepancies regarding marine contribution to global atmospheric cycling. Our empirical study shows that the older estimates were more in line with reality compared to the lower estimates. Furthermore, previous studies have ignored monsoonal inputs which we show to be very significant in depositional inputs of arsenic due to the volume of deposition associated with monsoons. Given that large tracts of the populated globe are in monsoonal regions, wet deposition is a major vector for arsenic inputs into terrestrial ecosystems.

The implications of oceans being a major source of arsenic now needs to be addressed; such as to how depositional inputs vary globally, temporally and what the impact of climate

change will have on deposition. Also, past atmospheric deposition may be a major contribution to the buried sediments that constitute groundwater arsenic stores as high arsenic in groundwaters are found in many delta regions with monsoonal climates (30). Intriguingly, Mirlean et al. (31) had hypothesized that the major source of ancient arsenic buried in coastal inter-dune swamps lacking fluvial contribution, are likely to be atmospheric in origin.

Associated content

Supporting Information

Details on the manufacturers of equipment and reagents, table of quality assurance data, including LoDs and CRM recoveries, tables with Spearman's correlation coefficient matrix for Bangladesh, Sri Lanka and combined sites elemental and speciation data, figures containing chromatograms for speciation analysis by both anion and cation IC-ICP-MS and regressions of arsenic species and trace element data for both sites with distances from 72-h weather trajectories.

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Legend to figures

Figure 1. The origin of 72-h weather trajectories modeled using Hysplit and arsenic speciation of monsoonal wet deposition for Bangladesh/summer (red) and Sri Lanka/winter (blue). The map was created using the Mac App Magic Maps.

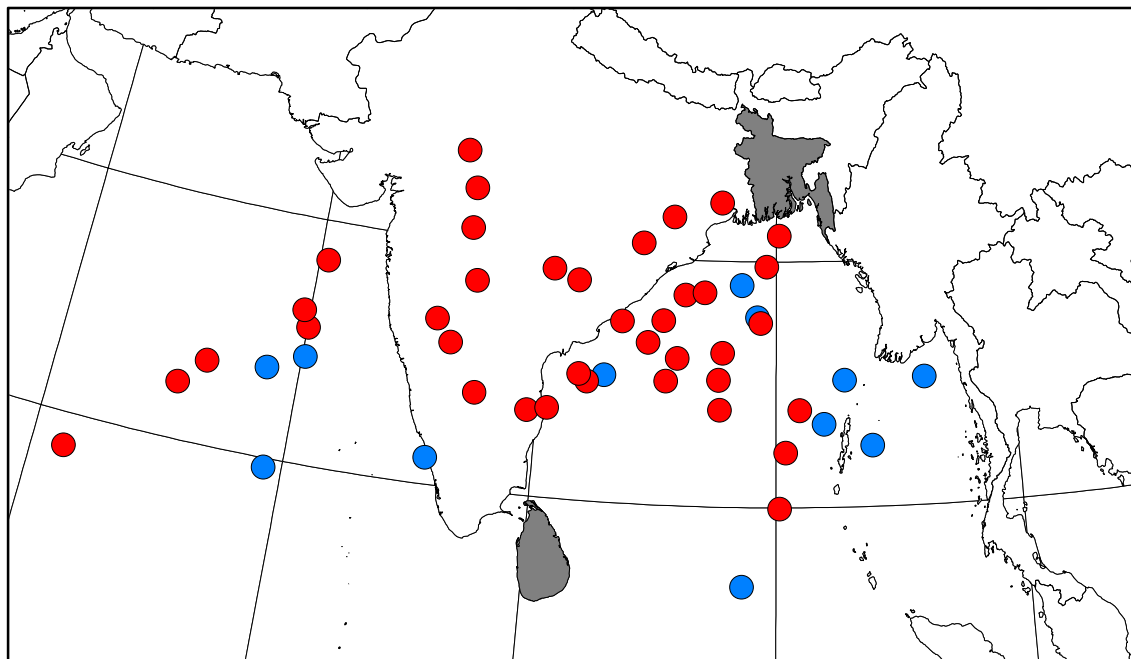


Figure 2. The individual daily wet deposition of arsenic species for Bangladesh samples collected from 01/04/2016 – 26/09/2016.

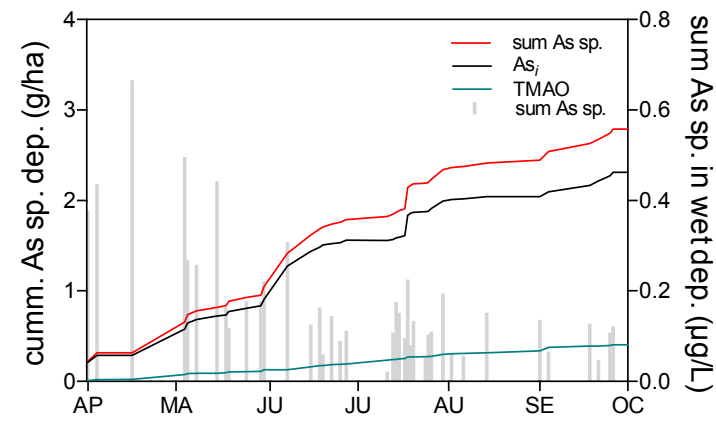


Figure 3. Relationship for both Sri Lankan (red triangles) and Bangladeshi (black circles) between TMAO and other elements/species.

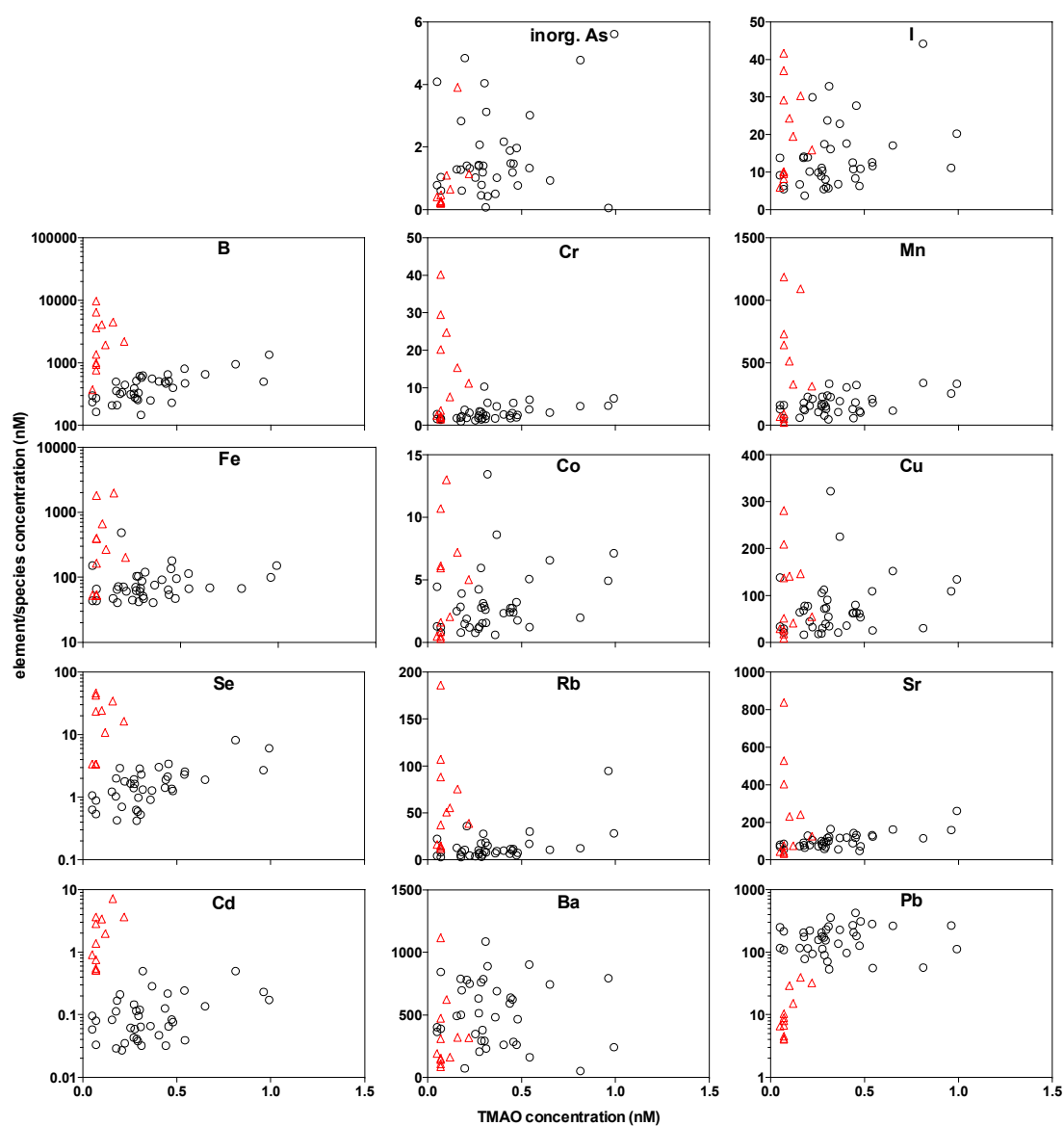


Figure 4. Relationship for both Sri Lankan (red triangles) and Bangladeshi (black circles) between inorganic arsenic and other elements/species.

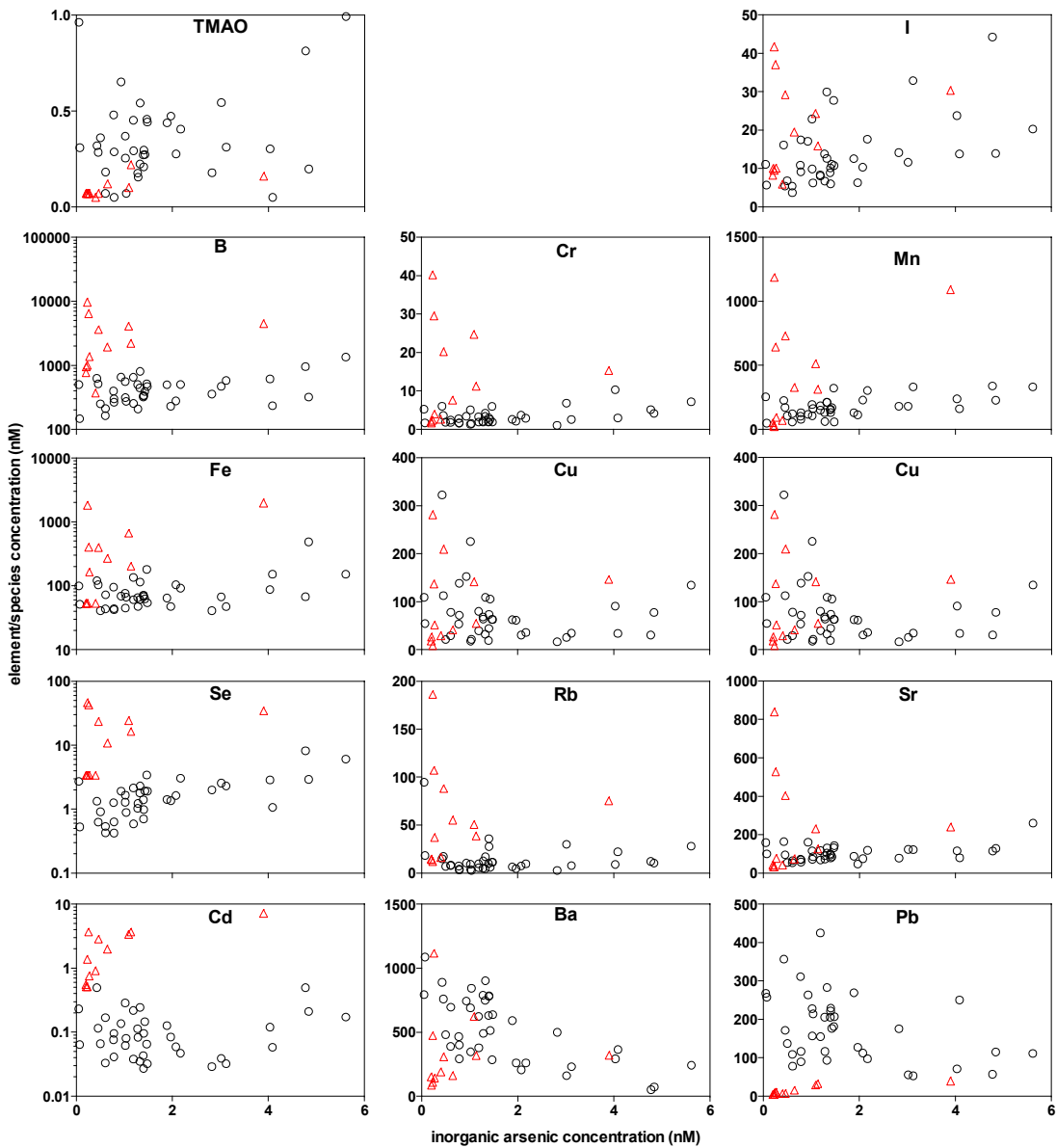


Figure 5. Relationship for both Sri Lankan (red triangles) and Bangladeshi (black circles) between deposition volume and elements/species.

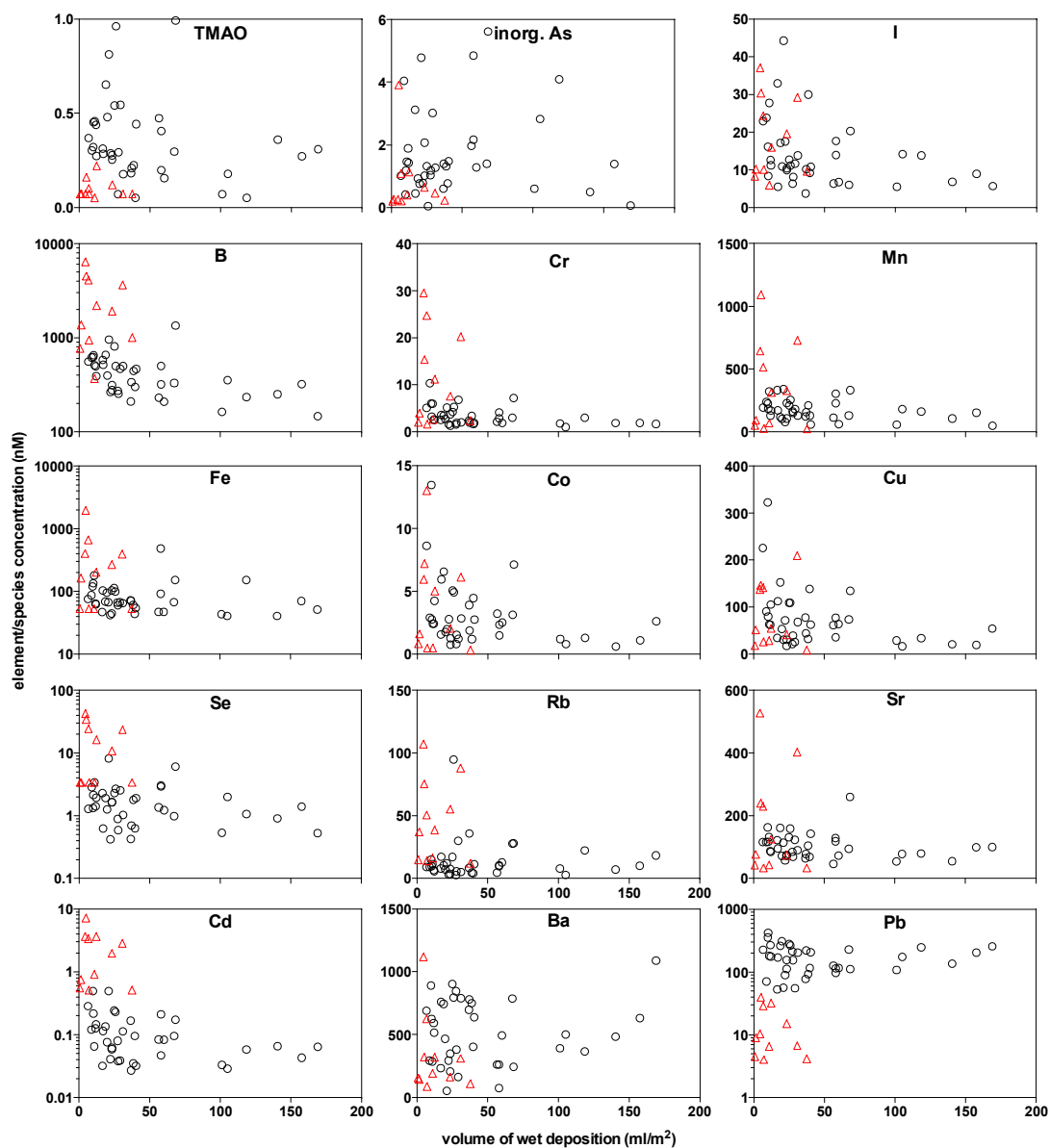


Figure 6. Principle components analysis Of Sri Lankan (red text, SL) and Bangladeshi (black text, B) elemental/species data (A), along with the factor loadings (B).

